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Combined *ab initio*/bond-valence method of pK_a prediction for oxide surfaces

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Standard surface complexation models often fail to describe the heterogeneity of surface functional group reactivity, and therefore are of limited applicability. Multisite complexation (MUSIC) models represent an attempt to describe the solid-solution interface in more detail, but require that the intrinsic pK_a values of surface functional groups be theoretically constrained.

Since it is difficult to experimentally distinguish between the contributions of different functional groups on a complex surface, the intrinsic pK_a values of such groups have usually been predicted by correlating the acidity of oxo- and hydroxo-solution species with some measure of the “unsaturated valence” on proton-reactive oxygen atoms, obtained by applying simple bond-valence methods. These correlations have then been applied to oxide surface functional groups [1].

A major flaw in these methods has been that bond relaxation, which can dramatically alter bond valences in solution monomers and surface functional groups, has not been considered. Therefore, we have correlated the acidity of oxo- and hydroxo- solution monomers with a measure of unsaturated valence that is derived from *ab initio* calculated structures of solution monomers [2]. These correlations were then used to successfully predict the acidity of surface functional groups on silica and gibbsite, using bond valences of proton-reactive oxygens derived from *ab initio* calculations of relaxed surface structures.

In addition, certain electrostatic effects were considered, including the ionicity of metal-oxygen bonds. This factor seems to be an indicator of how far the electrostatic field of the molecule or surface of interest deviates from that of a point charge or homogenous plane of charge, as is usually assumed in the calculation of “intrinsic” pK_a values.

References

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Influence of pH on the hydration state of Ca-montmorillonite: XRD profile modeling Vs chemical modeling

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Bentonite, a clay material constituted mostly of smectite, is considered a promising material for engineered barrier in the context of nuclear waste disposal. The potential of smectite as near-field engineered barrier material arises from the combination of mechanical self-healing ability, low hydraulic conductivity and high sorption capacities. The latter feature is expected to prevent or to delay the radionuclide migration. However, the initial properties of smectite could be significantly altered as a consequence of storage-induced perturbations. For example, the use of concrete for waste overpacks or the oxidation of pyrite which is often present as an accessory mineral in the geological environment can involve a wide pH-range in solutions in contact with the clay-barrier. In acid conditions the Ca^{2+}-H^+ exchange modifies the hydration state of smectite which is bihydrated when Ca-saturated and monohydrated when H^+-exchanged. Such a transition leads to a release of Ca^{2+} in solution and to hydration heterogeneities from one layer to the other resulting from the coexistence of layers with contrasting hydration states within a given crystallite.

This dual process has been investigated on the <2µm fraction of Swy-2, the Clay Minerals Society montmorillonite standard, following a 3 hour equilibration in pH-controlled conditions (0.1-12.6 pH range). The solution composition was monitored together with the interlayer composition and X-ray diffraction (XRD) patterns were recorded on oriented preparations. Experimental XRD patterns were then fitted using a trial-and-error procedure to quantify the relative proportions of layers with different hydration states.

At low pH, the proportion of monohydrated smectite layers determined from XRD profile modeling and that derived from chemical modeling (Phreeqc2 code) are strictly correlated. This correlation suggests that smectite layers are either H^+ or Ca^{2+} saturated and that the two species do not coexist in the same interlayer. In basic conditions, results from XRD profile modeling suggest that ionic pairs $Ca(OH)^+$ do not enter the interlayer space, and the apparent increase of Ca content in smectite interlayers is thus likely related to the precipitation of CSH phases.